CLAIMS

1. A process for preparing (per) fluorohalogenethers having general formula (II):

 $R'CF_2OCFA-CA'F_2$ (II)

wherein:

A and A', equal to or different from each other, are H, Cl or Br but they cannot be both H;

R' has the following meanings:

RO-, wherein R is a (per)fluorinated substituent, preferably perfluorinated, selected from the following groups: linear or branched C_1 - C_{20} alkyl, preferably C_1 - C_{10} ; C_3 - C_7 cycloalkyl; aromatic, C_6 - C_{10} arylalkyl or alkylaryl; C_5 - C_{10} heterocyclic or alkylheterocyclic;

when R is fluorinated, it optionally contains one or more atoms of H and/or one or more halogen atoms different from F;

when R is alkyl, cycloalkyl, arylalkyl, alkylaryl, alkylheterocyclic, it optionally contains in the chain one or more oxygen atoms;

a perfluoropolyether substituent $T-R_f$ wherein

 $T = -OCF_2OCFA-CA'F_2, -OCF_2X_I, \text{ wherein } X_I = F, CF_3, Cl;$ $R_f \text{ is a perfluorooxyalkylene chain containing one or}$

more of the following units statistically distributed along the chain:

- (C₃F₆O), selected between (CF₂CF(CF₃)O) or (CF(CF₃)CF₂O);
- (CFX₁O) wherein X₁ is F or CF₃;
- (C_2F_4O) ;
- ($CF_2(CF_2)_x$, CF_2O) wherein x' is an integer equal to 1 or 2;

by reaction of carbonyl compounds having formula (III):

R"COF (III

wherein

R" = RO-, wherein R is as above defined; or

 $R'' = Q-R_f-$ wherein:

Q = -OCOF, $-OCF_2X_I$ wherein X_I is as above defined;

 R_f is as above defined;

in liquid phase with elemental fluorine and with olefinic compounds having formula:

$$CAF=CA'F$$
 (IV)

wherein A and A' are as above defined, at temperatures from -120°C to -20°C, preferably from -100°C to -40°C, optionally in the presence of a solvent inert under the reaction conditions.

2. A process according to claim 1, wherein the fluorine used

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in the reaction is diluted with an inert gas.

- A process according to claims 1-2 carried out in a semicontinuous or continuous way.
- 4. A process according to claim 3, wherein in the semicontinuous process the molar ratio between the carbonyl
 compound (III) and the olefin (IV) ranges from 0.05 to
 10.
- 5. A process according to claim 3, wherein in the continuous process the molar ratio between the carbonyl compound (III) and the olefin (IV) ranges from 0.05 to 10 and the molar ratio F_2 /olefin (IV) ranges from 0.05 to 10.
- 6. A process according to claims 1-5, wherein the number average molecular weight of $R_{\rm f}$ in formula (II) and (III) ranges from 66 to 12,000, preferably from 66 to 1,000, more preferably from 300 to 800.
- 7. A process according to claim 6, wherein the perfluoro-oxyalkylene chains are selected from the following:
 - A) $-(CF_2-CF(CF_3)O)_m-(CFX_1O)_n-;$ wherein:

 X_1 is as above defined;

m and n are integers, equal to or higher than zero, and such that the molecular weight of $R_{\rm f}$ is in the above mentioned molecular weight range;

B) $-(CF_2CF_2O)_t - (CF_2O)_p - ;$

wherein t and p are integers, equal to or higher than zero, and such that the p/t ratio be in the range 0.2-4, t being different from zero and the molecular weight of $R_{\rm f}$ is within the above mentioned molecular weight range;

C) $-(CF_2CF_2O)_t - (CFX_1O)_n - (CF(CF_3)CF_2O)_m - ;$ wherein:

 X_1 is as above defined;

t, n, m are integers, equal to or higher than zero, and such that the molecular weight of $R_{\rm f}$ is within the above mentioned molecular weight range.

8. A process according to claim 7, wherein when R_f is structure A) the m/n ratio is ≥ 2 and n is different from zero;

when $R_{\rm f}$ is structure B), the p/t ratio is from 0.2 to 4, and t is different from zero;

when R_f is structure C), m + t is comprised between 1 and 50; the n/(m + t) ratio is comprised between 0.01 and 0.05, m + t being different from zero.

- 9. A process according to claims 7-8, wherein the perfluoro-oxyalkylene chain has structure B) $-(CF_2CF_2O)_t-(CF_2O)_p-$.
- 10. A process according to claims 1-9, wherein the carbonyl compounds of formula (III) are CF_3OCOF , C_2F_5OCOF , $CF_3O(CF_2)_2OCOF$.

11. A process according to claims 1-10, wherein the solvents are liquid and inert in the temperature range of the process reaction and are selected from (per)fluorocarbons, (per)fluoroethers, (per)fluoropolyethers, perfluoroamines, or respective mixtures.